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Some Double Halides of Zinc.

Thesis

Submitted to the Board of
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by.

Daniel Base.

1895.

71.269

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Introduction

Investigations in the field of double halides have been carried on in this laboratory since 1888, as a result of Professor Remsen's investigations[1] concerning the composition of double halides. "This law is based on the study of a large number of facts, namely over the four hundred compounds. The so called double compounds or salts, have been known for a long time, and at different times chemists have called attention to them and offered various explanations of their structure. On account of the difficulty of finding an explanation which did not conflict with the valence theory, chemists were for the most part content to pass the double salts by under the name of molecular compounds,

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[1] Amer. Chem. Jour. Vol. 11 - 291.

a term which conveys no more explanation with it than the term gravity does in the case of the ~~of the~~ falling of bodies to the earth.

The distinction between acidic and basic oxides has long been recognized, having been one of the factors which gave rise to the old "dualistic" or electro-chemical theory of Berzelius. A similar distinction between acidic and basic halides has also been made and this was first done by von Bonsdorff[1] who suggested that double halides were formed by the union of acidic with basic halides in the same manner in which acid oxides unite with basic oxides to form the so called true salts. About the same time Boullay[2] called attention to the same distinction and pointed out the similarity between the oxides, sulphides, chlorides, bromides, etc., and designated the compounds formed by the union of

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[1] Ann. Chim. Phys. 34, 142

[2] Ibid 34-337.

acid and basic halogen compounds as true salts, in contradistinction to molecular compounds. These views were held by some other chemists, notably Dr Hare[1] of Philadelphia. Liebig[2] and Berzelius[3] opposed this conception of double halides and because of their great influence the views of Von Bonsdorff and Boullay were not generally accepted, and the close analogy between double halides and oxygen salts was almost completely lost from view.

In 1889 Professor Remsen in an extended article brought forward again the whole subject and showed the close analogy between oxygen salts and halogen double salts, both in composition and the act of formation, and after studying 400 compounds or more, deduced the following generalization;

"When a halide of any element combines with a halide of an alkali metal to form a double salt

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[1] Compt. rend. [illegible]

[2] Ann. Chim. phys. 15, 68

[3] J. [illegible] 8, 135.

the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater, and is generally less than the number of halogen atoms contained in the latter".

To explain this regularity it was suggested that "two halogen atoms together can play the same part that the so-called linking oxygen atom plays in the oxygen salts", thus,

$Al{-}OK$ $Al{-}Cl_2K$ or $AlCl_3{\cdot}KCl$.

This explanation had been proposed many years before, first by Naquet[1] in 1861. The same view was held by Blomstrand,[2] Jörgensen,[3] Mallet[4] [illegible][5], Hayes[6] and others. Thus this idea of two halogen atoms taking the place of one oxygen atom was not a new one, but it had not hitherto met with general acceptance, chiefly because the evidence in its favor had never been fully presented. The principal

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[1] Principes de chimie fondée sur les théories modernes. Par A. Naquet

[2] Chemie der Jetztzeit.

[3] J. Prakt. Chem. 16, 352.

[4] Amer. Chem. Journ. 189

[5] J. prakt. Chem. (N.F.) 36, 457

[6] Phil. mag. 25, 221, 297

objection to this theory which comes from Horstmann is suggested by the theory of constant valence and the univalence of the halogen atoms. But as nearly all chemists today accept the view of variable valence of the halogens, the objection of Horstmann loses its weight and it can safely be said that the views of Professor Remsen are pretty generally accepted. The investigations on double halides that have since been carried out, have for their purpose the testing of the law of composition of these salts, and the verification of the views as to their structure, that two chlorine atoms play the part of a bivalent group and have a linking function.

Over against the 200 compounds or more which come under the law, there are a few exceptions which require an extension. The exceptions have been reduced to a small number. The two oldest longest known are $CuCl.2KCl$ and $CdCl_2.4KCl$. Recently Wells and Walden[1], and Wells and Campbell[2]

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1. Amer. Jr. Sc. Dec. 1893
2. Ibid

have brought out new compounds which cannot be explained under the old form of the law. These are,

$CdBr_2 \cdot 3CsBr$. $ZnCl_2 \cdot 3CsCl$.
$CdI_2 \cdot 3CsI$. $ZnBr_2 \cdot 3CsBr$.
$ZnI_2 \cdot 3CsI$.

To explain these an extension of the law has been made, which is that just as two chlorine atoms can play the part of a bivalent group, so three chlorine atoms together can play the part of a trivalent group. This view is expressed thus, $-Cl<^{Cl-}_{Cl-}$ and $CuCl_2 \cdot 2KCl$ is written, $Cu-Cl<^{Cl-K}_{Cl-K}$.

None of the salts described in this investigation fall under this extension of the law.

In recent years a new field has been opened in the study of double halides in that salts have been made containing organic aromatic bases, chiefly aniline and the toluidines instead of inorganic bases, as one of the constituents of the double salt. Swan in 1893 and Slagle —

1899, both working in this laboratory, studied respectively the double salts of mercury and tin with the aromatic bases. Their results were in accordance with the law as first put forth.

This is not strictly a new field, for numerous examples of double salts with organic bases have been recorded but these were not made with a view of bearing out or refuting any principle, such as the theory of double salts, and in no case was a thorough study made, the only object being to get a salt of the organic halide with an inorganic one for the sake of better characterizing the organic compound.

To continue the investigation of double halides containing organic bases, it seemed desirable to study the double salts of zinc with aniline and the toluidines, an account of which is given in this paper. As the halides of the organic bases are closely related to the ammonium halides,

and as a number of zinc ammonium double chlorides are recorded in the literature, some of which do not ~~agree with~~ conform to the laws and the authority for which might be questioned, it seemed best at the same time to make a study of these compounds. This work will be spoken of in the latter part of this paper.

All the double salts of zinc with inorganic as well as organic halides that have been recorded in the Jahresberichte up to 1888 inclusive and in the other journals up to the present, have been collected and tabulated. For the sake of completeness, I thought it well to give these salts with the references.

Double Chlorides.

$ZnCl_2 \cdot 2NH_4Cl \cdot H_2O$	J 12, 148	Schindler.
" "	Ann. Chem. pharm. LXVI, 280	Hautz.
" $\cdot NH_4Cl \cdot 2H_2O$	" " " " "	"
" $2NH_4Cl$	Pogg Ann. XCIV, 507	Rammelsberg.

$ZnCl_2 . 2NH_4Cl$ Ann. des Mines (5) 12. 1. Marignac

" $3NH_4Cl$ " " " " " " "

" $2NH_4Cl \cdot H_2O$ } Ann. Chim. phys. Berthelot and André

" $6NH_4Cl \cdot \frac{1}{3}H_2O$ }

" $4NH_4Cl$ Bl. 1861, 51 Dehérain

" $2KCl$. Pogg Ann. XCIV, 507 Rammelsberg.

" " Ann. des Mines (5) 12. 1, Marignac.

" $2NaCl . 3H_2O$ " " " " " " "

" $BaCl_2 \cdot 4H_2O$ } J. 1873, 273 G. Werner.

" $MgCl_2 . 6H_2O$ }

" $3CsCl$ } Amer. Jr. Sc. Dec. 393 Wells & Campbell.

" $2CsCl$ }

" $PtCl_2 . 6H_2O$ J 1877, 312 Nilson.

" $PtCl_4 \, 6H_2O$ } J. 1870, 393. Topsoë

" $PdCl_4 \, 6H_2O$ }

" $2(AuCl_3) . 8H_2O$ J 1874, 177 Topsoë

" " $12H_2O$ Pogg. Ann. 17, 261; 33, 64: Bonsdorff.

" $2AuCl_3$ " " " " " " "

Double Chlorides with Organic Constituent.

$ZnCl_2$ · 2($C_7H_4N_2$·HCl. Cyanconiine) Jr. prakt Chem. (2) 33, 70. E. v. Meyer

" 2(C_9H_7N·HCl. Quinoline) B. 1882, 646. Wallach.

" 2(Tetramethyl triamido triphenyl carbinol·2HCl) J. 1883, 675 Döbner.

" (p-amido-o-imido-phenylurea) B. 1884, 2625. Hager.

" (Quinine·3HCl) + H_2O J. 1885, 1701. Comstock & Königs

" 2(papaverin.HCl) J 1885, 1697. Goldschmiedt.

" (β-picolin HCl.) B 1885, 3091. Ad. Hesekiel

" 2(α-γ-dimethylquinoline·HCl) J 1886, 935. C Beyer.

ZnI_2·2(papaverin·HCl) J 1886, 1716. Jahoda.

$ZnCl_2$·2.(Ethyl triamidonaphthalin·HCl.) Chem. Soc. J. 11. [illegible] & [illegible]field.

" (cinchonine.2HCl) B. 1887, 2510 Comstock & Königs

" 2(C_5H_5N·HCl.) B 1888, 1578. Lang.

" (dipyridin.2HCl) Chem. Soc. Jr. (2) VII, 406. Anderson.

Double Bromides.

$ZnBr_2 \cdot 2CsBr$ } (Amer. Jr. Sc. Dec. 1893. Wells & Campbell.
,, · $3CsBr$ }

,, · $2NH_4Br$ J 1860, 17.

3 ,, $2DiBr_3 \cdot 36H_2O$ J 1878, 245. Frerichs & Smith.

3 ,, $DiBr_3 \cdot 12H_2O$ J 1885, 481 P.T. Cleve.

3 ,, $2LaBr_3$ $39H_2O$ Ann. Chem. 191, 331

$ZnBr_2 \cdot PtBr_4 \cdot 12H_2O$ J 1868, 274. Topsoë.

Double Iodides,

$ZnI_2 \cdot 2NH_4I$ J, 1[illegible], 2[illegible], Rammelsberg.
,, KI ,, ,, ,,

,, · $2NaI \cdot 3H_2O$,, ,, ,, ,,

2 ,, BaI_2 ,, ,, ,, ,,

$ZnI_2 \cdot As(CH_3)_4I$ (old formula) J 1859, 431. Cahours.
· $As(C_2H_5)_4I$,,

,, $P(C_2H_5)_4I$. J. [illegible], [illegible].

$P(C_2H_5)_3 \cdot HI$,, ,, ,,

$ZnI_2 \cdot BiI_3 \cdot 12HO$ (old formula) J. 1860, 178, [illegible]

3 " · 2 DiI_3 $24H_2O$ J 1878, 245. Frerichs & Smith.

3 " $2LaI_3 \cdot 27H_2O$. " " " " " "

$ZnI_2 \cdot PtI_4 \cdot 9H_2O$ J. 1870, 389. Topsoë

" · $2CsI$ Amer. jr. sc. Dec. 1893, Wells & Walden.

" · $3CsI$ " " " " " "

Double Fluorides.

$ZnFl \cdot SiFl_2 \cdot 6HO$. (old formula.) J 1859, 108 Marignac

$ZnFl_2 \cdot TaFl_5 \cdot 7H_2O$ J 1866, 204. "

" · $SnFl_4$ $6H_2O$ J 1859, 112 "

" · $2KFl$. Pogg Ann. I, 26. Berzelius.

" · Al_2Fl_6 " " " " "

" · KFl. B. 1886, 896. Wagner

" $NaFl$ " " " " "

" $2NH_4Fl, 2H_2O$ " " " " "

" $2BFl_3$ " " " "

2 $ZnFl_2 \cdot Mn_2Fl_6 \cdot 8H_2O$ J 1886, 420 Christensen

It will be seen that some of the compounds recorded above do not come under the law of the composition of double halides, or the extension of the law. However it would be necessary to repeat the work before accepting these few exceptions as speaking against the law. One of the ammonium zinc double chlorides recorded was apparently an exception, but by repeating the work it was possible to obtain only two double ammonium salts, both of which fall under the law or its extension.

The materials used were prepared in the usual way. Zinc chloride and bromide were made by dissolving zinc in the respective acids. Ammonium chloride was sublimed.

Method of analysis; The salts were analyzed for zinc, halogen, and water of crystallization when present. Zinc was precipitated as carbonate, and weighed

as oxide. (Treadwell II. p. 250). The organic bases had no solvent action on the zinc carbonate, as ammonium salts have when present in the solution.

Chlorine was determined gravimetrically or volumetrically by Volhard's method.

Compounds described.

$ZnCl_2 \cdot 2C_6H_5NH_3Cl \cdot H_2O$ Dianiline chlorozincate,
$ZnCl_2 \cdot 3C_6H_5NH_3Cl \cdot 2H_2O$ Trianiline chlorozincate.

$ZnCl_2 \cdot 2C_6H_4<^{CH_3\ (o)}_{NH_3Cl} \cdot 2H_2O$ Diorthotoluidine chlorozincate.
$ZnCl_2 \cdot 2C_6H_4<^{CH_3\ (m)}_{NH_3Cl}$ Dimetatoluidine chlorozincate
$ZnCl_2 \cdot 3C_6H_4<^{CH_3\ (m)}_{NH_3Cl}$ Trimetatoluidine chlorozincate.

$ZnCl_2 \cdot 2C_6H_4<^{CH_3\ (p)}_{NH_3Cl}$ Diparatoluidine chlorozincate
$ZnCl_2 \cdot 3C_6H_4<^{CH_3\ (p)}_{NH_3Cl}$ Triparatoluidine chlorozincate

$ZnBr_2 \cdot 2C_6H_5NH_3Br \cdot H_2O$ Dianiline bromozincate.
$ZnBr_2 \cdot 2C_6H_4<^{CH_3\ (o)}_{NH_3Br} \cdot H_2O$ Diorthotoluidine bromozincate
$ZnBr_2 \cdot 2C_6H_4<^{CH_3\ (m)}_{NH_3Br} \cdot 2H_2O$ Dimetatoluidine bromozincate
$ZnBr_2\ 3C_6H_4<^{CH_3\ (m)}_{NH_3Br}$ Trimetatoluidine bromozincate

$ZnBr_2 \cdot 2C_6H_4<^{CH_3\ (p)}_{NH_3Br} , H_2O$ Diparatoluidine bromozincate.

$ZnCl_2 \cdot 2NH_4Cl$ Diammonium chlorozincate
$ZnCl_2 \cdot 3NH_4Cl$ Triammonium chlorozincate.

Double Chlorides.

Dianiline chlorozincate $ZnCl_2 \cdot 2C_6H_5NH_3Cl \cdot H_2O$.

This salt was made by H. Vohl,[1] in 1865, in an indirect way. In an article, "On the compounds of zinc chloride with aniline and the application of the same in the arts," Vohl describes the preparation of the salt $ZnCl_2 \cdot 2C_6H_5NH_2$. It forms according to him shining white needles, decomposed by water and obtained from alcohol. In dilute hydrochloric acid the compound is easily soluble and yields a new compound crystallizing in large colorless columnar crystals and plates, which become colored to a violet blue in contact with the air. This salt is easily soluble in alcohol and water. It contains water of crystallization which escapes completely at 105° Centigrade. Heated more strongly it melts, vapors of aniline hydrochloride are formed, while zinc chloride remains behind, which takes on a violet blue color.

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1. Ding. Pol. jr CLXXV; 211.

This description of the double salt by Vohl was found to be correct, and his analyses were good, showing the salt to have the formula as written above.

His object in making the double salt was to prepare aniline dyes, in accordance with the method in use at that time. By mixing the double salt with an oxidizing agent, as mercurous nitrate, and heating, fuchsine was formed. Vohl made no systematic study of double salts nor had he any idea of getting more than one aniline salt, and therefore a repetition of the work in a thorough manner is justified especially as the object now is to get evidence for or against the law of composition of double salts. My work has shown that there are two double aniline salts, one being identical with that described by Vohl.

When zinc chloride and aniline hydrochloride are mixed so that the number of molecules of

the proportions of the latter bear these relations, 3:1, 2:1, 1:1, 1:2, dianiline chlorozincate is formed in every case. It seems to make no difference whether the solutions are heated or not, or whether they are neutral or made acid. The solutions soon change color to a red brown or greenish color, even when mixed in the cold. The ease with which they become colored varies with the proportion of aniline hydrochloride present. Alcoholic solutions color extremely rapidly. On standing, a flocculent greenish material is formed in the solutions. The shape of the crystals varies with conditions. The most frequent form is the plates spoken of by Vohl. The plates belong to the triclinic system[1]. The salt is easily purified by recrystallization from water. When pure it does not change color readily in the air. It loses all its water in the sulphuric-acid desiccator,

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[1] Examined by Mr Arthur Spencer of this University.

the weight remaining constant after transferring to an air-bath and heating up to 100°degrees. It is extremely soluble in methyl alcohol, so much so that it cannot be recrystallized from it. It is less soluble in Ethyl alcohol.

.457 grm Salt. gave .0904 gr. ZnO. and .6365 gr. AgCl.
.3912 " " " .0772 " " " .5408 " "
.4405 " " lost .0191 " Water.

Calculated for.		Found 1	2
$ZnCl_2 . 2C_6H_5NH_3Cl \cdot H_2O$.			
	Zn 15.77	15.81	15.82.
	Cl. 34.32	34.3	34.18.
	H_2O. 4.357	4.34	

* * *

Trianiline Chlorozincate $ZnCl_2 . 3C_6H_5NH_3Cl \cdot 2H_2O$ -

When zinc chloride and aniline hydrochloride are brought together in water solution so that the molecular proportions of the former to the latter are as 1:3, 1:4, 1:6, trianiline chlorozincate is formed. The 1:3 mixture yields the dianiline salt also, which can easily be separated

from the trianiline salt on account of its totally different crystal form.

The solutions soon become deeply colored, but the crystals are colored only a little, and by washing with water, are good enough for analysis. By recrystallizing from water, they are colorless and pure. The salt is more soluble in water and alcohol than the dianiline salt. It is stable in the air but on long exposure, changes color to a green. It loses all its water of crystallization in the sulphuric acid desiccator, and can be heated in the air-bath to 100°C without decomposition. It forms long prisms apparently of the ortho-rhombic system. The prism forms are unit prism and macro prism.

.3538 gr. Salt gave .051 gr. ZnO and .4536 gr. $AgCl$.
.2875 " " " .042 " " " .369
.[illegible] — lost .0[illegible]3 gr. H_2O

Calculated for	Found.	
$ZnCl_2.3C_6H_5NH_3Cl.2H_2O.$	1	2
Zn. 11.62	11.57	11.74
Cl. 31.58	31.7	31.75
H_2O 6.41	6.52	

The two salts described were the only ones that it was possible to obtain by varying the proportions of zinc chloride and aniline hydrochloride.

Diortho toluidine chlorozincate, $ZnCl_2.2C_6H_4\overset{CH_3.H_2O}{NH_3Cl}$ – This compound was prepared in 1865 by Trakinhoff[1], who made a study of the action of the toluidines (ortho and para) on zinc chloride. He was led to this study by the work of Vohl, referred to in connection with the dianiline salt. His object was the same as Vohl's, that is, the preparation of compounds of zinc chloride with toluidine for technical application in the preparation of dyes. On treating the toluidine compound with hydrochloric acid, drying on the water-bath and taking up with

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[1] J. prakt. chem. (1866) XCV, [illegible]

alcohol, he says he obtained the salt $ZnCl_2 \cdot 2(C_7H_9N \cdot HCl)$. This salt, he says, can also be prepared directly from zinc chloride and toluidine hydrochloride; and when obtained from water solution contains water of crystallization, but when obtained from alcohol, it contains no water. He says further, "to avoid the objection that the existence of these salts was shown only for the liquid toluidine, toluidine was prepared out of pure toluene from Tolu balsam, which according to Muspratt and Hofmann, was solid. Salts were formed in the same manner and analyzed and their identity with those from the liquid toluidine shown. They agreed in solubility and physical properties perfectly with the latter".

Gräfinghoff's object evidently was not to make a systematic study of double halides.

Bibanow[1] also says he obtained from a mixture of orthotoluidine hydrochloride and a concentrated

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[1] Mon. Scient. [3] 4 - 925

zinc chloride solution, by cooling down to $-5°C$. a salt of the composition $ZnCl_2 \cdot 2C_6H_4{}^{CH_3}NH_3Cl$, having no water of crystallization; and forming colorless concentrically grouped plates.

Zinc chloride and orthotoluidine hydrochloride were brought together in aqueous solution in the molecular proportions 3:1, 2:1, 1:1, 1:2, 1:4, In the last case the toluidine hydrochloride separated out first. The solutions were heated to boiling and it mattered not whether they were made acid or not. They did not change color nearly so rapidly as the aniline zinc-hydrochloride solutions, and deposited very little of the green flocculent material.
Only one salt was obtained from all these mixtures, as was shown by analysis, the same as was obtained by [illegible]. The salt is colorless when pure, but gradually becomes colored when exposed to

the air. It gives off water and takes it up again, according to the temperature and hygroscopic state of the atmosphere. Solutions of the salt easily become supersaturated, and, in strong solutions, the salt crystallizes out in long, concentrically grouped plates, as described by Bibanow. The plates are striated, so that they have a sort of hour-glass appearance. They lose all their water of crystallization over sulphuric acid, and can be heated in the air-bath up to 130° without decomposition. When heated high enough, the salt melts to a brown liquid from which toluidine hydrochloride sublimes.

As the salt loses water easily, it must be pressed between filter-paper, powdered, and not allowed to lie long in the air before analysis.

.2775 gr. Salt. lost .0024 gr. Water.

.2021 " " gave .0359 " ZnO and .2539 gr. AgCl.

.351 [illegible]

Calculated for $ZnCl_2 \cdot 2C_6H_4{}^{CH_3}NH_3Cl \cdot 2H_2O$		Found 1	 2
Zn	14.42	14.26	14.43
Cl	30.86	31.06	31.16
H_2O	7.83	8.07	

Metatoluidine chlorozincate, $ZnCl_2 \cdot 2C_6H_4{}^{CH_3}NH_3Cl$. – This salt is formed when the constituents are brought together in the molecular proportions 3:1; 2:1. It forms fine, silken needles, which are extremely soluble in water. They cannot be washed, but must be sucked dry on the filter-pump, and pressed between filter-paper. Owing to the nature of the crystals and their great solubility, it is very difficult to get a specimen of the salt pure so as to give sharp analyses. The results are not as good as could be desired ~~better~~ but they are close enough to show that the compound has the formula given above.

.0941 gr salt gave .0187 gr. ZnO and .03187 gr. Cl.

.1917 " " " .0377 " " " .2568 " AgCl.

Calculated for $ZnCl_2 \cdot 2C_6H_4 \begin{smallmatrix} CH_3 \\ NH_3Cl \end{smallmatrix}$	Found 1	2
Zn 15.42	15.95	15.8
Cl. 33.48	33.87	33.13

These results were from different specimens.

Trimetatoluidine chlorozincate, $ZnCl_2 \cdot 3C_6H_4 \begin{smallmatrix} CH_3 \\ NH_3Cl \end{smallmatrix}$. – Mixtures of zinc chloride and metatoluidine hydrochloride were made in aqueous solution in the proportions of 1:1, 1:2, 1:4. All these gave the same double salt, the tritoluidine chlorozincate. The solutions soon assume a red purple color, and the crystals are nearly always colored. When pure, they are colorless. The salt crystallizes in fine needles, which grow in radiating tufts and are not as soluble as the ditoluidine salt, but still are too soluble to be washed with water, and must be sucked

dry and pressed between drying paper. In this way the salt was obtained in pure condition for analysis.

.1394 gr. salt. gave .0201 gr. ZnO and .1751 gr. AgCl
.1929 " " " .028 " " " .2426 " "
.2225 " " " .0316 " " " .278 " "

Calculated for $ZnCl_2 \cdot 3C_6H_4{<}^{CH_3}_{NH_3Cl}$		Found 1	2	3
Zn	11,5	11,57	11,65	11,4
Cl	31,24	31,06	31,14	30.72

* * *

Diparatoluidine chlorozincate $ZnCl_2 \cdot 2C_6H_4{<}^{CH_3}_{NH_3Cl}$.— This salt was referred to under the corresponding orthotoluidine salt. Träjinghoff said he prepared the salt at the same time that he made the ortho salt. He did not give any analyses nor did he state whether only one salt could be formed, or more than one. There are two para salts, while only one ortho salt could be made.

Diparatoluidine chlorozincate is formed when

zinc chloride and the toluidine hydrochloride are mixed in the proportions 3:1, 2:1, 1:1, 1:2, 1:3. The solutions were heated to boiling and made slightly acid. The salt crystallizes in colorless plates which form a matted mass.

The solutions color very slowly. They cannot be purified by boiling with boneblack as they become colored more, to a deep purple.

The crystals have various forms, sometimes being triangular plates, sometimes triangular plates with the angles truncated.

The salt is easily soluble in cold water. It is stable in the air, and does not change color.

.2567 gr. salt gave .0487 gr. ZnO and .3482 gr. AgCl.
.2743 " " " .0524 " " " .3707 " "

Calculated for $ZnCl_2 \cdot 2C_6H_4 <^{CH_3}_{NH_3Cl}$	Found 1	2
Zn 15,42	15,3	15,37
Cl. 33.48	33.54	33.44

Triparatoluidine chlorozincate, $ZnCl_2 \cdot 3C_6H_4<^{CH_3}_{NH_3Cl}$. –

This salt is formed when zinc chloride and paratoluidine hydrochloride are brought together in water solution in the proportions 1:3, 1:4. The 1:4 mixture ~~separates out~~ deposits the organic solids ~~as~~ first ~~crop~~. Sometimes the ditoluidine salt is formed in the 1:3 mixture. There is this tendency at low temperatures. At a slightly elevated temperature, only the 1:3 salt is formed.

The salt is a well-crystallized compound belonging apparently to the triclinic system and resembling ~~the~~ albite crystals in outline. The forms are, $0P$, $\bar{P}'\infty$, $\infty{,}'P$, $\infty P'{,}$, $\infty\breve{P}\infty$.

.191 gr. salt gave .0273 gr. ZnO. and .2406 gr AgCl

.2483 " " " .0354 " " " .315 gr. AgCl.

Calculated for $ZnCl_2 \cdot 3C_6H_4<^{CH_3}_{NH_3Cl}$.	Found – 1	2
Zn. 11.5	11.[illegible]	11.[illegible]
Cl. 31.24	31.15	31.37

Double Bromides.

Dianiline bromozincate, $ZnBr_2 \cdot 2C_6H_5\text{-}NH_3Br \cdot H_2O$. –

Aniline hydrobromide behaves a little differently from the corresponding chloride, in that it separates out as such from mixtures in which the proportion of aniline hydrobromide to zinc bromide is greater than 2:1. A 3:1 mixture could not be made as in the case of the chloride. Addition of hydrobromic acid caused a still greater separation of the organic halide. Only one double salt could be obtained from all the different mixtures. It seemed to be that formed in a 1:1 solution. Sometimes a solution of 1 molecule of zinc bromide to two molecules of organic halide would ~~separate out~~ deposit. the organic halide along with the double salt. The salt crystallizes in thick prismatic plates resembling those of the corresponding

double chloride, and probably belonging to the same system.

The solutions remain colorless, differing again in this respect from those of the corresponding chloride. The salt cannot be recrystallized from water, as aniline hydrobromide separates out. It is easily soluble in cold water. It loses its water of crystallization on heating and does not decompose at 110°.

.2452 gr. salt gave .0345 gr. ZnO and .3112 gr. AgBr.
.2249 " " " .0318 " "
.2609 " " " .3315 " "
.1758 " " lost .0052 gr. water.

Calculated for		Found		
$ZnBr_2 \cdot 2C_6H_5NH_3Br \cdot H_2O$		1	2	3.
Zn	11.02	11.30	11.35	
Br	54.19	54.00		54.06
H_2O	3.05	3.24.		

Orthotoluidine bromozincate, $ZnBr_2(C_6H_4\overset{CH_3}{NH_2}HBr)_2H_2O$. —

Orthotoluidine hydrobromide is like the chloride in its behavior towards zinc bromide, that is, it does not separate out as such from mixtures in which it is present in excess, as the aniline hydrobromide does. Mixtures were made in many proportions, but only one salt could be obtained. The solutions color slowly. The salt can be recrystallized from water, and forms large colorless prismatic plates. It can be heated in the air-bath to 120° without decomposition, and, when heated to 150°, it begins to melt to a blue liquid, giving off vapors of toluidine hydrobromide. The salt is readily soluble in cold water.

.2364 grams salt gave .0337 grm ZnO and .31 gr. AgBr
.6305 " " " .0852 " " .7663 " "
.3802 " " lost .0117 water.

Calculated for. $ZnBr_2\cdot 2C_6H_4{<}^{CH_3}_{NH_3Br}\cdot H_2O$	Found. 1.	2.
Zn. 10.52	10.56	10.85
Br. 51.70	51.45	51.72
H_2O 2.90	3.08	

* * *

Dimetatoluidine bromozincate, $ZnBr_2\cdot 2C_6H_4{<}^{CH_3}_{NH_3Br}\cdot 2H_2O$.

This salt is formed in solutions which contain zinc bromide in excess, i.e., in 3:1, 2:1, or 1:1 solutions. The salt is with difficulty obtained in pure condition, as there is a strong tendency to the formation of a tritoluidine salt, to be described presently. Sometimes in these mixtures, one crop of crystals will be the ditoluidine salt, the next crop a tritoluidine salt, and the third a ditoluidine salt again. The ditoluidine salt forms long thick prismatic bars. The solutions soon become colored, and the crystals are nearly always more or less colored.

The salt loses its water in the [illegible] and can be heated above 100° without decomposing.

.2647 gr. Salt gave .0336 gr. ZnO and .3128 gr. AgBr.
.2184 " " " .0275 " " " " .2581 " "
.2647 " " lost .0148 gr. water.

Calculated for: $ZnBr_2 \cdot 2C_6H_4{CH_3 \atop NH_3Br} \cdot 2H_2O$	Found 1	2
Zn. 10.23	10.28	10.11
Br. 50.20	50.27	50.28
H_2O. 5.64	5.59	

Trimetatoluidine ~~hydrobromide~~ bromozincate $ZnBr_2 \cdot 3C_6H_4{CH_3 \atop NH_3Br}$.

Of the two metatoluidine double salts this one is most easily formed, being produced in solutions containing an excess of zinc bromide as well as in those in which the toluidine hydrobromide is in excess. It crystallizes in long needles or prisms, for the most part colored purple. By pressing between filter paper, they are fit for analysis.

.2291 gr. Salt. gave .0237 gr. ZnO and .11575 gr. Br.
.2663 " " " .0287 " " " .1341 " Br.

Calculated for. $ZnBr_2\cdot 3C_6H_4\cdot\overset{CH_3}{NH_3Br}$	Found — 1.	2.
Zn 8.26	8.30	8.47
Br. 50.71	50.52	50.54

These two meta salts are much less soluble in cold water than the corresponding chlorine salts. It was not possible to wash the latter without dissolving the crop of crystals, while the former can be washed clean on the filter pump.

Diparatoluidine bromozincate, $ZnBr_2\cdot 2C_6H_4\cdot\overset{CH_3\cdot H_2O}{NH_3Br}$.

When solutions of zinc bromide and paratoluidine hydrobromide are made in the proportions of 1:1, 1:2, 1:3, the paratoluidine hydrobromide crystallizes out without forming a double salt. Addition of hydrobromic acid causes more of the

organic halide to separate out. In this respect, the behavior is like that of aniline hydrobromide. Mixtures containing zinc bromide in excess, for example, 2:1, 3:1, yield a double salt, crystallizing in large thin shining colorless leaves. These were filtered off, sucked dry and pressed between paper. When washed with water the crystals become opaque at once, evidently being decomposed. On trying to recrystallize the salt from water, it is broken down, yielding crystals of paratoluidine hydrobromide. The salt is stable in the air and does not change color.

.2122 gr. Salt. gave .0283 gr. ZnO
.1495 " " – .1826 gr. AgBr.
.255 " " " .0345 gr. ZnO and .3107 "
.2302 " " lost .0072 " water.

Calculated for	Found 1	2	3	4.
$ZnBr_2 2C_6H_4{\cdot}^{CH_3}_{NH_3Br}{\cdot}H_2O$				
Zn 10.52	10.71		10.86	
Br 51.70		51.97	51.84	
H_2O 2.9				3.12

Double ammonium zinc chlorides.

As was stated in the beginning of this paper, the close relationship between ammonia and the organic bases made it desirable to investigate the double zinc-ammonium chlorides, along with those of the organic bases, especially since a number of them are recorded, in regard to some of which a doubt may arise as to their existence. The following salts are recorded.

1 $ZnCl_2 \cdot 2NH_4Cl \cdot H_2O$. Schindler, J. 12, 148; also Hautz, Annalen, LXVI p. 287. The latter says he obtained the salt from one part ammonium chloride and two parts zinc chloride.

2. $ZnCl_2 \cdot NH_4Cl \cdot 2H_2O$ Hautz, loc. cit. He mixed one part of each constituent and obtained this salt in large shining leaves, as he says.

3. $ZnCl_2 \cdot 2NH_4Cl$. Rammelsberg. Pogg. Ann. XCIV, 507.

Also Marignac, Ann. des Mines [5] 12, 1.

4. $ZnCl_2 \cdot 3NH_4Cl$. Marignac loco cit.

5 $ZnCl_2 \cdot NH_4Cl$. } Dehérain, Bl. 1861, 31,
6 $ZnCl_2 \cdot 4NH_4Cl$. } says that $ZnCl_2 \cdot NH_4$, $ZnCl_2 \cdot 2NH_4$, $ZnCl_2 \cdot 4NH_4$ when dissolved in hydrochloric acid, yield corresponding double chlorides.

7. $ZnCl_2 \cdot 6NH_4Cl \cdot \frac{2}{3}H_2O$ } Berthelot and André,
8 $ZnCl_2 \cdot 3NH_4Cl \cdot H_2O$ } Ann. chim. phys. (6) 11, 294-310. These chemists mention the existence of these two salts but do not state how they are obtained.

By working under various conditions, I was able to obtain only two double salts, namely nos. 3 and 4 in the list above, which were also obtained by Marignac. He did not make a thorough study, but made a mixture in only one molecular proportion.

As these salts were completely described by Marignac, I cannot do better than to give his own words. He says: "In his treatise on crystallographical chemistry, Rammelsberg describes the crystal forms of this salt, u.s.3) to which he attributes the formula $ZnCl_2 \cdot 2NH_4Cl$. An earlier analysis by Schindler made it appear to contain an equivalent of water, and it is to be noticed that the crystals described by Rammelsberg may be regarded as isomorphous with the stannous ammonium chloride described by the same chemist and of which he represents the composition by the formula $SnCl_2 \cdot 2NH_4Cl \cdot H_2O$. These considerations have induced me to undertake again the examination of these salts. The results have not answered to what I supposed, but they are not the less curious. They prove in effect the existence of two double salts, both anhydrous and represented

by the formulas, — see 3 and 4 above.

What is most singular is that these two salts, perfectly distinct as regards their appearance and their faces, have forms which can be derived from ~~each other~~ one another. However, we cannot call them isomorphous since they do not mix in any wise in crystallizing, and there is no passage from the one to the other, although they are found sometimes simultaneously in the same beaker."

Marignac calls, $ZnCl_2 \cdot 2NH_4Cl$ the laminated salt, and $ZnCl_2 \cdot 3NH_4Cl$ the prismatic salt. He dried the salts in all cases at 100°, at which temperature they preserved their transparency and lost only a trace of hygroscopic water. The prismatic crystals are right rhombohedral prisms.

ammonium chlorozincate,

$ZnCl_2 \cdot 2NH_4Cl$. —

Mixtures of zinc chloride and ammonium chloride

were made in the molecular proportions of 3:1, 2:1, 1:1, 1:2. The same salt was obtained from all of them, the laminated salt of Marignac. It formed large shining plates. Sometimes a 1:2 mixture gave the 1:3 salt, (prismatic) at first, and the 1:2 salt in later crops. The mixtures were neutral or made slightly acid.

.2125 gr substance gave .0711 gr. ZnO and .5036 gr AgCl
.1891 " " " .0632 " " " " " "
.2456 " " " " .5776 " "

Calc. for $ZnCl_2 . 2NH_4Cl$	Found 1	2	3
Zn 26.[illegible]3	26.86	26.84	—
Cl 58.32	58.60	—	58.16

Ammonium chlorzincate,

$ZnCl_2 . 3 NH_4Cl$.

Solutions of zinc chloride and ammonium chloride in the proportions of 1:3 and 1:6 gave only the 1:3 salt. In the 1:6 solution, ammonium chloride crystallized out first.

.1546 gr. salt gave .04[illegible] gr. ZnO and .[illegible]59 gr AgCl.
.4685 " " " .1272 " " " 1.1267 "

Calc. for $ZnCl_2 \cdot 3NH_4Cl$.		Found. 1	2
Zn	22.00	22.02	21.80
Cl	59.76	60.13	59.47

Solutions of zincchloride and ammonium chloride were made in the proportions of 1:1 and 1:4, in concentrated hydrochloric acid in order to see if the strong acid would cause the formation of salts different from those just described. The first crop of crystals from the 1:1 solution was the 1:3 salt of Marignac, as was shown by their appearance and analysis. The other crops were composed of plates which proved to be the 1:2 salt. The 1:4 solution gave the 1:3 salt.

Dehérain says that when $ZnCl_2 \cdot NH_3$, $ZnCl_2 \cdot 2NH_3$ are dissolved in hydrochloric acid corresponding double chlorides are formed.

According to Kane[1], $ZnCl_2 \cdot 4NH_3 \cdot H_2O$ is formed when concentrated ammonia is added to a hot concentrated zinc chloride solution until the precipitate first formed is dissolved. On cooling, the salt is said to separate out in small brilliant plates with pearly lustre. According to Marignac[2], $ZnCl_2 \cdot 2NH_3$ is often formed at once when the two solutions are brought together as described by Kane. Kane says that, on further evaporation of the solution after removing the first crop of crystals, $ZnCl_2 \cdot 2NH_3 \cdot \frac{1}{2}H_2O$ crystallizes out in radiating groups of square prisms of a brilliant vitreous lustre. $ZnCl_2 \cdot NH_3$ is obtained, according to Kane by heating $ZnCl_2 \cdot 4NH_3H_2O$ or $ZnCl_2 \cdot 2NH_3 \cdot \frac{1}{2}H_2O$, ammonia and water being given off, and a gummy mass being left behind.

Following Kane's directions, as [illegible], a compound was obtained the analysis of which gave results agreeing fairly well with.

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1 A. ch. [2] 72, 290   2 Ann. des mines (5) 12, 1.

[illegible]

the formula $ZnCl_2 \cdot 3NH_3 \cdot H_2O$. The determination of zinc was less than ~~different from~~ the theoretical per cent, by 1.6%. Some of this compound was dissolved in hydrochloric acid and allowed to crystallize. Small prismatic crystals were obtained that resembled in all respects the 1:3 salt described by Marignac. A determination of zinc was made, .2397 gr. salt giving .0647 gr. ZnO. i.e 21.74. Theoretical per cent for the 1:3 salt is 22.00.

On heating the rest of the compound $ZnCl_2 \cdot 4NH_3 \cdot H_2O$, ammonia was given off, and a gummy mass was left, as described by Kane. This was dissolved in hydrochloric acid, and allowed to crystallize. Thin shining plates were formed looking exactly like the 1:2 salt already described. It seems then that dissolving these compounds in hydrochloric acid is equivalent to making solutions of zinc chloride and ammonium chloride

in the proportions of 1:4 and 1:1 and we have seen that the former solutions yields a 1:3 salt while the latter yields a 1:2 salt.

In conclusion it may be said that all the salts described in this paper come under the law of double halides or the extension of the law.

$ZnCl_2 \cdot 3C_6H_5NH_3Cl \cdot 2H_2O$

$ZnCl_2 \cdot 3C_6H_4 \genfrac{}{}{0pt}{}{CH_3\ (m)}{NH_3Cl}$

$ZnCl_2 \cdot 3C_6H_4 \genfrac{}{}{0pt}{}{CH_3\ (p)}{NH_3Cl}$

$ZnBr_2\ 3C_6H_4 \genfrac{}{}{0pt}{}{CH_3\ (m)}{NH_3Br}$

$ZnCl_2 \cdot 3NH_4Cl$

are the salts which fall under the extension.

The author of this paper was born in Baltimore, Md., September 6, 1869. After attending the public schools, he entered the Baltimore City College from which he graduated in 1888. In the same year he entered the Johns Hopkins University, graduating as A.B. in 1891. Since then he has been pursuing a post-graduate course in Chemistry, Physics and Mathematics.